Correlation Properties Of Inhomogeneous Substance Under Gravity Close To The Critical Point[1]

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ABSTRACT

The correlation peculiarities for inhomogeneous liquid under gravity close to the critical point were investigated by the light scattering method. On the basis of data of high-altitude and temperature dependencies of light scattering intensity I(h,t) the surfaces and three projections for correlation length $R_c(h,t)$, fluctuation part of free energy $\Delta F(h,t)=C_0R_c^{-3}(h,t)$ and probability of fluctuations creation $w(h,t)=\exp(-\Delta F/k_bT)$ in field h – temperature t – property (R_c, ΔF, w) coordinates were calculated and constructed. Here $t=(T-T_c)/T_c$, $h=\rho_c g\Delta z/P_c$; T_c , ρ_c , P_c are critical temperature, density and pressure , Δz is height indicated from the critical density level of sample cell, g - terrestrial acceleration. Conclusions are made as follows: 1. Temperature dependencies $R_c(t)$, $\Delta F(t)$, w(t) at t>0 and fixed heights $\Delta z\neq 0$ are nonmonotonous. Extremum magnitudes of the values correspond not to critical temperature T_c but to limit critical direction – susceptibility extremum line. Only at $\Delta z=0$ the dependencies are monotonous. 2. Surface $\Delta F(h,t)$ determines the surfaces of thermodynamic values: density $\Delta\rho(h,t)=dF/d\mu=dF/dh\cdot dh/d\mu$, where $d\mu/dh\approx 10^2$ is for freon-113, n-pentane, and solution n-pentan – benzol [1]; entropy $s(h,t)=dF/dt$; heat capacity $C_\mu(h,t)=d^2F/dt^2$; compressibility $\beta_T(h,t)=d^2F/d\mu^2\sim R_c^{2-\eta}$; coefficient of thermal expansion $\alpha= d^2F/(dtd\mu)$ and others determined values. These properties are connected with existence of susceptibility extremum line. 3. Probability of fluctuations creation w(h,t) at the equal "distances" h for susceptibility extremum line when going far away from the critical point is less than for critical isochor and is more than for phase interface.

KEY WORDS: correlation length; effect of gravity; free energy; ; inhomogeneous liquid; critical opalescence; critical point; phase transitions; fluctuation

1. INTRODUCTION

Earlier, in work [1,2] at investigation of high-altitude and temperature dependences of light scattered intensity I (h,t) in inhomogeneous substance near critical point (CP) under gravity the unusual, on the face of it, non-monotone temperature dependence I (t) at heights $h = \rho_c gzP_c^{-1} \neq 0$ (here ($t = (T - T_c)T_c^{-1}$ was detected; T_c, ρ_c, P_c are critical temperature, density and pressure, g - gravity acceleration, z - height digitized from the critical density level ($\rho=\rho_c$). It has appeared, that at these heights the light scattered intensity in inhomogeneous substance reaches the greatest value not at critical temperature but at $T > T_c$. The theoretical analysis of this appearance was carried out in [1] within the framework of the fluctuation theory of phase transition [3].

The purpose of present investigation was continuation of these experimental investigations I (h,t) near to the susceptibility extremum line, study of correlation properties of inhomogeneous substance under gravity in close vicinity of the critical point.

2. MEASUREMENTS

For this purpose were analyzed the data of high-altitude and temperature dependence of light scattered intensity I (h, t) near CP a liquid - vapor for individual substances (freon - 113, pentane, diethyl ether) [4-6]. Then these data used for the analysis of correlation properties for inhomogeneous substance under gravity near liquid-vapor CP.

Based on the fluctuation theory of phase transition [3], the thermodynamic properties of liquid system near CP are defined by a fluctuation part of a free energy

$$F=C_0R_c^{-3} \qquad (1)$$

(R_c is correlation length). From relation (1), based on equations of substance state near critical point, it is possible to draw a conclusion, that just correlation properties of substance (behavior R_c) define its manifold thermodynamic properties near critical point. The information on $R_c(z, t)$ behavior can be obtained from data on high-altitude and temperature dependences of critical opalescence with usage I (z, t) in form [7]:

$$R_c(z,t) = \frac{1}{k}\left[\left(\frac{I_c}{I(z,t)}\right)^{1+\frac{\eta}{2}} - 1\right]^{-\frac{1}{2}} \qquad (2)$$

Where I_c is light scattered intensity at angle of 90 degrees at the critical point (z=0 and t=0); $k=4\pi/\lambda \sin\theta/2$ - transmitted wave vector; $\eta=0,06$ [3,8].

3. RESULTS

Based on (2) and using obtained in paper [4] data of light scattered intensity for inhomogeneous fluids freon - 113, pentane, diethyl ether the three-dimensional surfaces of correlation length $R_c(z,t)$ and fluctuation part F(z,t) of free energy are calculated and constructed.

For example we shall analyze these surfaces in individual substance freon - 113 $C_2F_3Cl_3$ (threefluorthreeclorethane).

3.1. Temperature and field dependences of correlation length for inhomogeneous substance under gravity.

In fig.1.1. the surface $R_c(t,h)$ is shown. This surface is built with (2) on data I(h,t) for inhomogeneous freon - 113 under gravity in close vicinity of critical point. For its analysis we shall esteem its three projections in planes R_c-t, R_c-h, t-h.

3.1.1.

In fig 1.2. the projection of a three-dimensional surface $R_c(t,h)$ on a plane R_c-t, that is temperature dependence $R_c(t)$ is figured at stationary values h. From a fig. visual, that dependencies of symmetrized values $\overline{R_c(t)}$ (for identical on an absolute value of heights $h > 0$ and $h < 0$ $\overline{R_c(t)} = [R_c(t, h > 0) + R_c(t, h < 0)] /2$) are nonmonotone functions of temperature: the maximum value $R_c(t)$ corresponds not critical temperature, but temperatures $T_{max}>T_c$ ($t_{max} > 0$). These maximum values of dependences $R_c(t)$ form a line of extremum of correlation length. From a fig. 1.2. it is shown, that at identical values of temperature |t| $R_c(t<0,h=0) < R_c(t_{max},h_{max}) < R_c(t>0,h=0)$. The analysis of presented data reveals, that along a critical isochor $R_c(t) = 3{,}8\ \mathring{A}\ t^{-\nu}$, along a phase interface $R_c(t)=1{,}8\ \mathring{A}\ t^{-\nu}$, along the line of extremum $R_c(t)= \mathring{A}\ t^{-\nu}$. That is the quantity of correlation length on the extremum line takes intermediate value between quantity of correlation length on a phase interface and critical isochor. From a fig. follows also, that at identical heights values |h| $R_c(t_{max},h_{max})=1{,}3\ \mathring{A}\ h^{-\xi} > R_c(t=0,h)=1\ \mathring{A}\ h^{-\xi}$. That is the quantity of correlation length on the extremum line is larger, than on critical isotherm.

3.1.2.

In a fig.1.3. the high-altitude dependences of symmetrized values $R_c(h)$ are shown at $T < T_c$ and $T > T_c$. At $T < T_c$ (fig. 1.3.A) dependences $R_c(h)$ lay one under one and are not intersected anywhere. At $T > T_c$ (fig.1.3.B) dependences $R_c(h)$ are intersected, that just is consequence of existence of the extremum line.

3.1.3.

In a fig. 1.4. the third projection of the three-dimensional diagram - line of identical values R_c in coordinates t and h is shown. These lines also are lines of constant values of a compressibility $\beta_T=Ar_c^{2-\eta}$. They are nonmonotone in range

$t > 0$: at first increases with temperature, the maximum value reaches, and then wanes. The line of extremum of correlation length is schematically figured by a dashed line. It corresponds to points on lines h(t), where a derivative $(dh/dt)\ R_c$=const =0. From a fig. it is shown, that in coordinates (h, t) the range, restricted by line R_c=const at $t > 0$ is significant larger, than at $t < 0$. This implies a deduction, that at $t > 0$ fluctuation range of parameters (h, t) are much more, than one at $t < 0$.

3.2. Fluctuation part of a free energy of inhomogeneous system under gravity.

On datas $R_c(h, t)$ fig.2.1. the quantity of a fluctuation part of a free energy of system in one mole of substance $F/P_cV_c=F^*=C_0R_c^{-3}$ ($C_0=10^{-22}$ sm^3 was calculated [9]), This quantity is equal to work of fluctuations formation [10] $A^*=A/P_cV_c$ near CP. The obtained results $F^*(h, t) = A^*(h,t)$ are given in a fig. . The fluctuation part of system free energy defines also probability w of fluctuations formation [10] $F^*(h,t)/\ _BT= - \ln w$ near CP.

3.2.1.

In a fig. 2.2. the projections of a surface F*(h,t) on a plane (F*,t) for a phase interface (h=0, t < 0), critical isochor (h=0, t > 0) and relevant line of extremum of fluctuation part of system free energy are shown. From the figure one can see, that at identical temperatures |t| $F^*(t>0,h=0)<F^*(t_{max},h_{max})<F^*(t<0,h=0)$. That is the work of fluctuations formation on a line of extremum takes intermediate value between its value on a critical isochor and phase interface. The probability of fluctuations formation on a line of extremum also takes intermediate value between its value on phase interface and critical isochor (at identical |t| $w(t<0,h=0)<w(t_{max},h_{max})<w(t>0,h=0)$).

3.2.2.

In a fig. 2.3. the projections on a surface F*(h, t) of critical isotherm and line of extremum on a plane (F*,h) are shown. One can see, that at identical |h| $F^*(t=0,h)>F^*(t_{max},h_{max})$. That is work of fluctuations formation on a critical isotherm larger, than on extremum line. Probability of fluctuations formation on extremum line larger, than on a critical isotherm (|h| $w(t_{max},h_{max})>w(t=0,h)$).

3.2.3.

In a fig. 2.4. the third projection of a surface F*(h,t) of work of fluctuations formation on a plane (h, t) is shown. One can see, that at t > 0 identical values of work of fluctuations formation take considerably larger (h, t) parameters range, than one at t < 0.

3.3. Thermal and caloric equations of state.

Based on this surface of system free energy, knowing its equation F*(h,t) under gravity, it is possible to construct thermal and caloric equations of state for inhomogeneous substance under gravity for entropy $\Delta s=(\partial F\ /\partial t)_{\mu}$, density $\Delta\rho=(\partial F\ /\partial\mu)_{t}$, compressibility

$\beta_T \sim (\partial^2 F\ /\partial\mu^2)_T$, heat capacity $_{\mu v}\sim(\partial^2 F\ /\partial t^2)_\mu$, thermal expansion coefficient $\alpha_t \sim (\partial^2 F\ /\partial t \partial\mu)$ and of other related with them quantities.

Thus, usage of experimental data on critical opalescence in spatial inhomogeneous systems under gravity enables to study of behaviour both correlation, and manifold thermodynamic properties of inhomogeneous fluids under gravity in close vicinity of critical point.

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FIGURE CAPTIONS

Fig. 1.1 Surface of correlation length in coordinates temperature - height

Fig. 1.2. Projection of surface of correlation length to a plane R_c-t

Fig. 1.3.A. Projection of surface of correlation length to a plane R_c-h, $t < 0$

Fig. 1.3.B. Projection of surface of correlation length to a plane R_c-h, $t > 0$

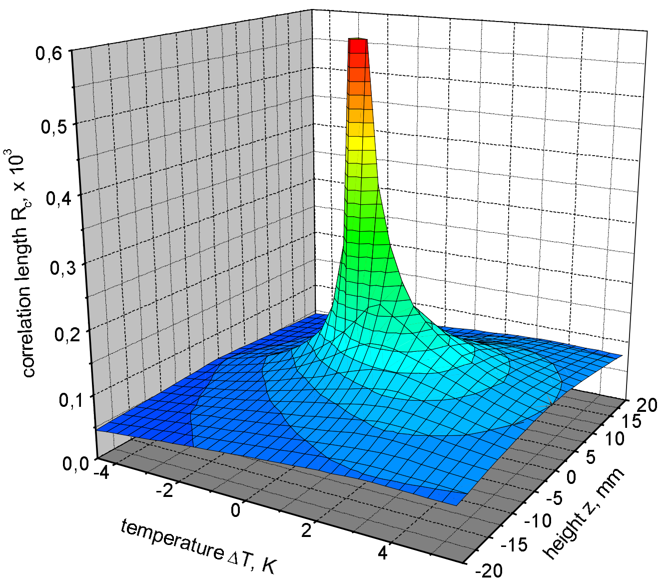
Fig. 1.4. Projection of surface of correlation length to a plane h-t

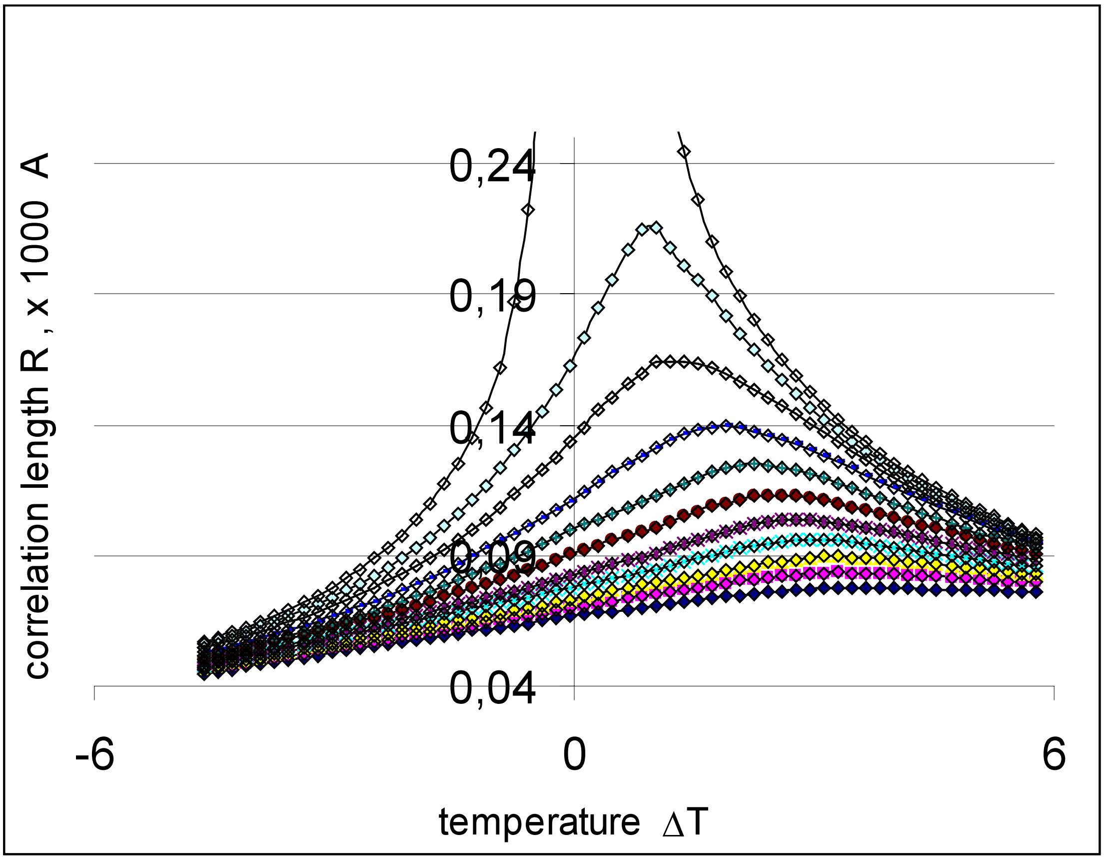
Fig. 2.1. Surface of free energy in coordinates temperature - height

Fig. 2.2. Projection of surface of free energy to a plane R_c-t for critical isochor, phase interface, line of free energy extremum

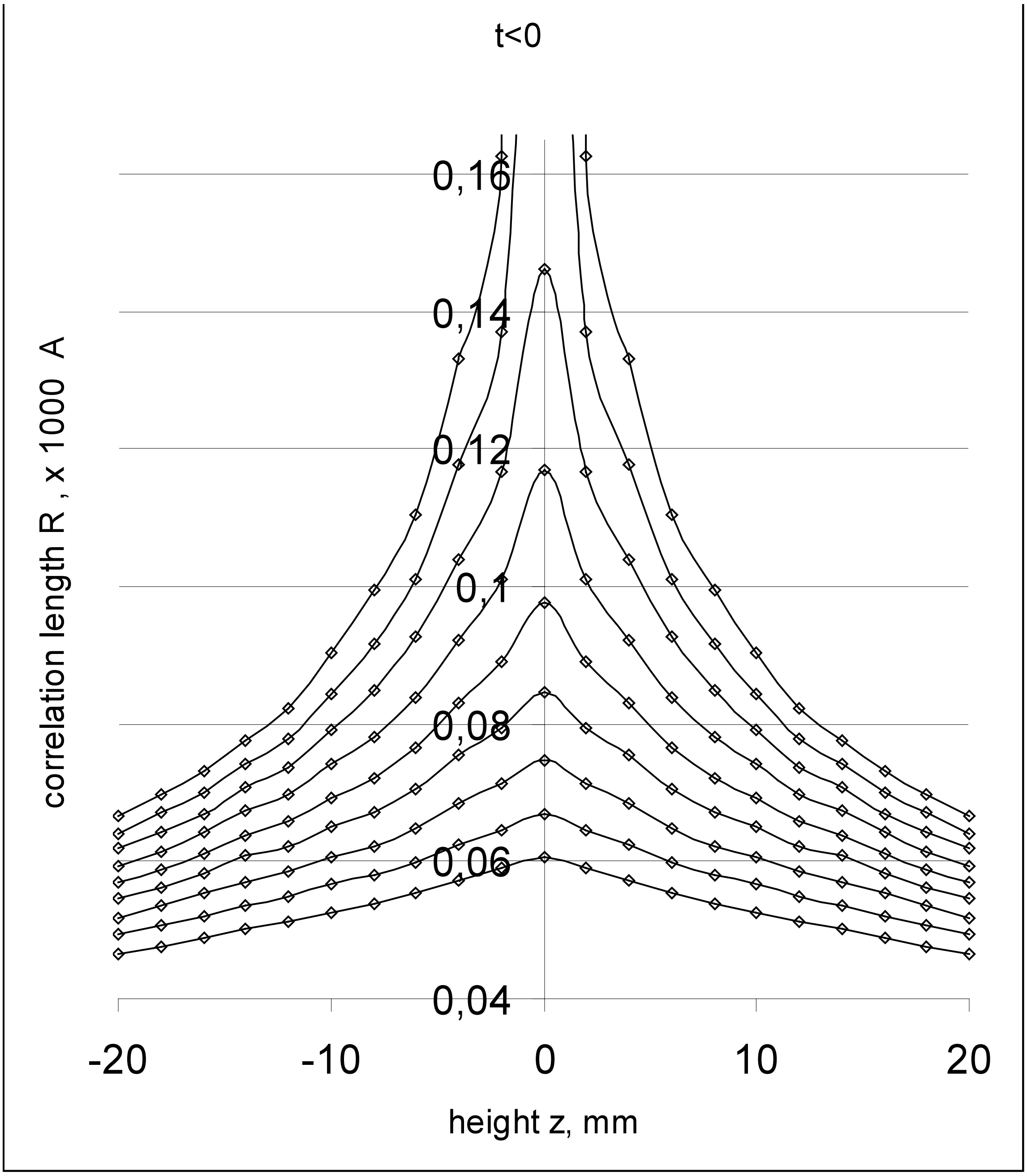
Fig. 2.3. Projection of surface of free energy to a plane R_c-h for critical isotherm, line of free energy extremum

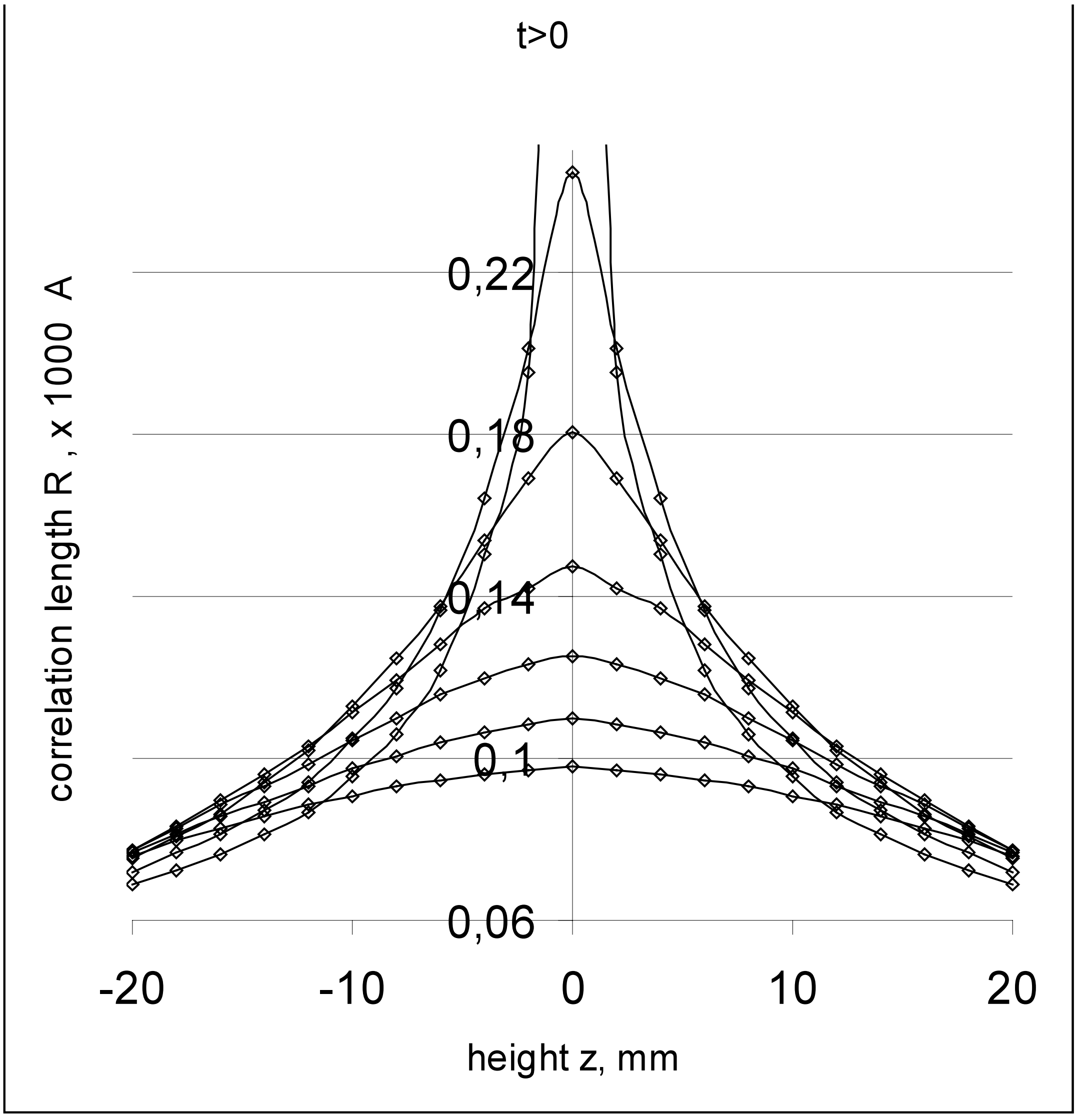
Fig. 2.4. Projection of surface of free energy to a plane h-t


correlation length R_c, x 10^3
0,6
0,5
0,4
0,3
0,2
0,1
0,0
-4
-2
0
2
4
temperature ΔT, K
20
15
10
5
0
-5
-10
-15
-20
height z, mm



correlation length R , x 1000 A
0,24
0,19
0,14
0,09
0,04
-6
0
6
temperature ΔT


t<0
correlation length R , x 1000 A
0,16
0,14
0,12
0,1
0,08
0,06
0,04
-20
-10
0
10
20
height z, mm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0,14
0,1
0,06
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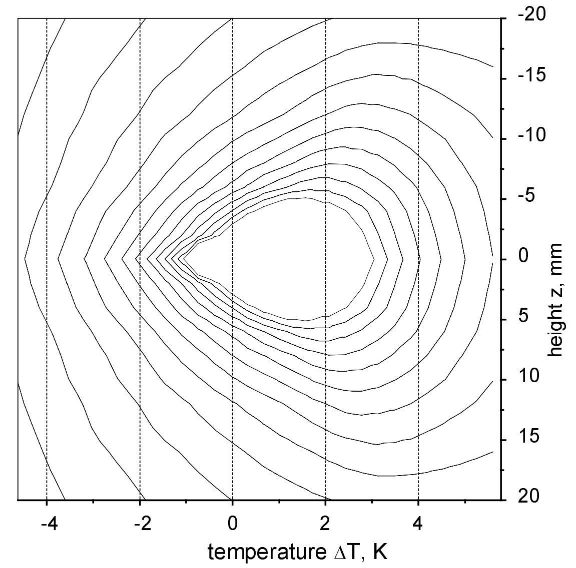
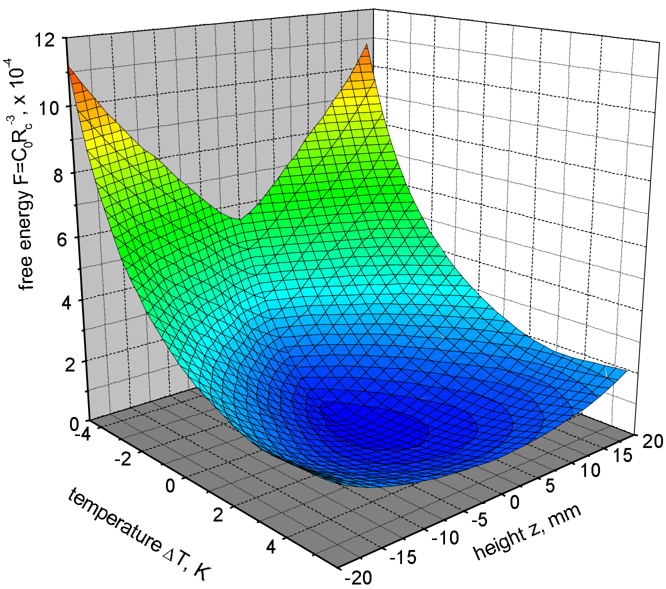
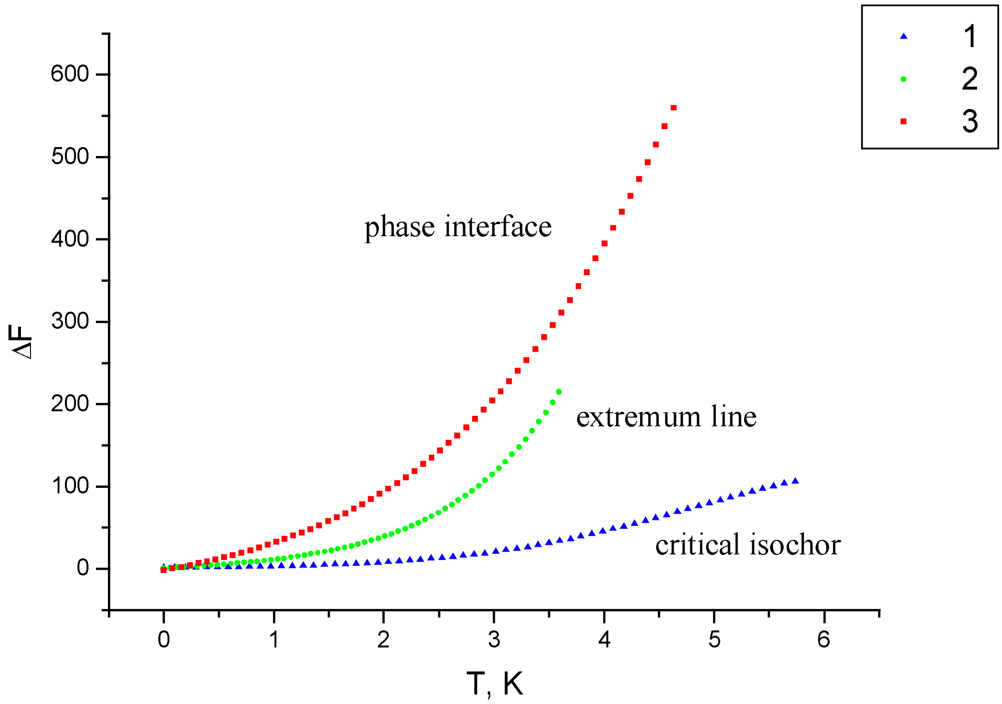
-10
0
10
20
height z, mm



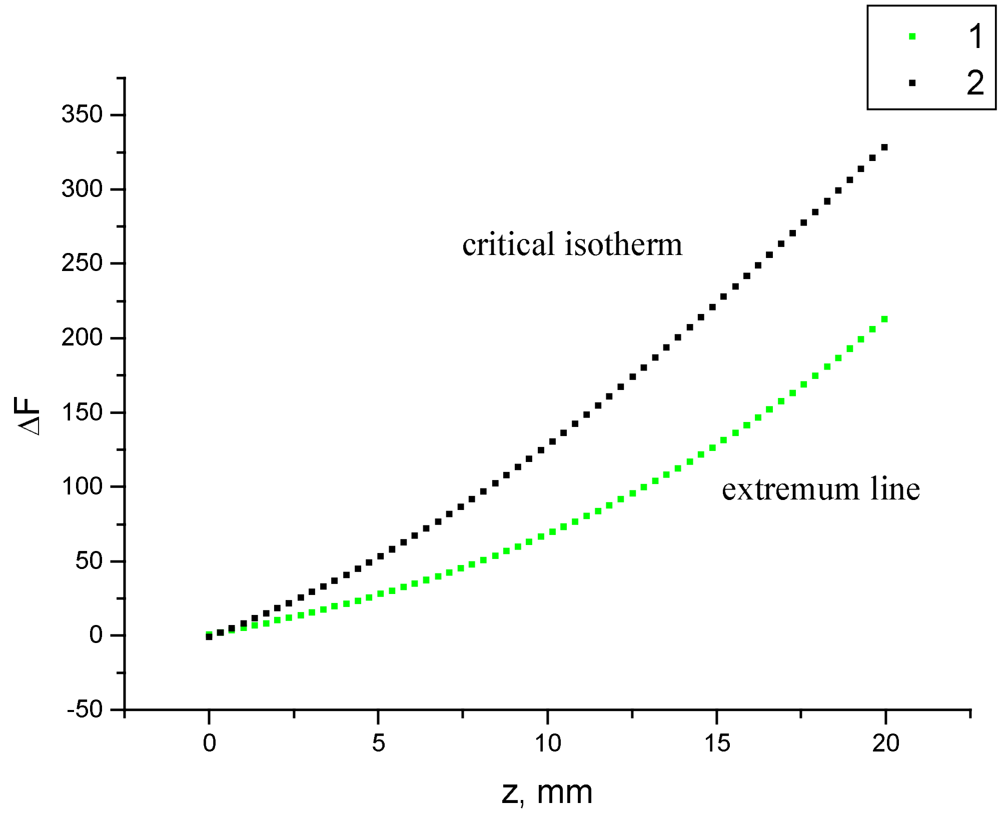
-20
-15
-10
-5
0
5
10
15
20
height z, mm
-4
-2
0
2
4
temperature ΔT, K

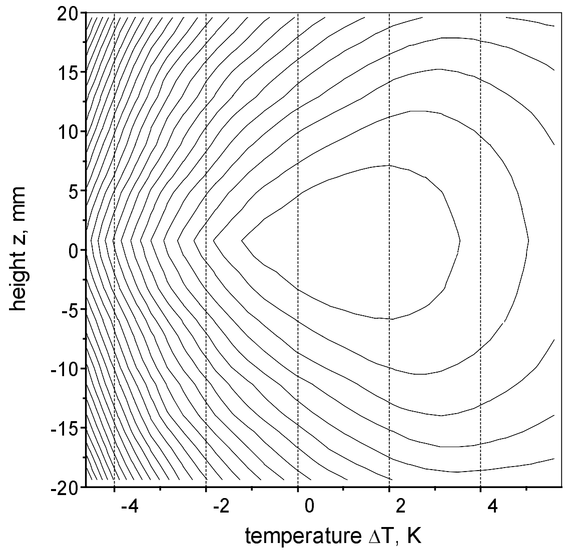


free energy $F=C_0R_c^{-3}$, x 10^{-4}
12
10
8
6
4
2
0
-4
-2
0
2
4
temperature ΔT, K
-20
-15
-10
-5
0
5
10
15
20
height z, mm



1
2
3
600
500
400
300
200
100
0
ΔF
phase interface
extremum line
critical isochor
0
1
2
3
4
5
6
T, K


1
2
350
300
250
200
150
100
50
0
-50
ΔF
critical isotherm
extremum line
0
5
10
15
20
z, mm



20
15
10
5
0
-5
-10
-15
-20
height z, mm
-4
-2
0
2
4
temperature ΔT, K